13. Rotational and Vibrational Spectroscopy

After studying this lecture, you will be able to do the following:

Calculate the bond lengths of diatomics from the value of their rotational constant.

Outline the selection rules for rotational and vibrational spectra and rationalize the role of the molecular dipole moment in the selection rules.

Distinguish between the energy levels of a rigid and a non rigid rotor.

Distinguish between harmonic and anharmonic vibrations.

Sketch qualitatively rotational-vibrational spectrum of a diatomic.

Calculate the relative populations of rotational and vibrational energy levels.

Identify the IR frequencies where simple functional groups absorb light.

13.1 Introduction

Free atoms do not rotate or vibrate. For an oscillatory or a rotational motion of a pendulum, one end has to be tied or fixed to some point. In molecules such a fixed point is the center of mass. The atoms in a molecule are held together by chemical bonds. The rotational and vibrational energies are usually much smaller than the energies required to break chemical bonds. The rotational energies correspond to the microwave region of electromagnetic radiation (3×10^{10} to 3×10^{12} Hz; energy range around 10 to 100 J/mol) and the vibrational energies are in the infrared region (3×10^{12} to 3×10^{14} Hz; energy range around 10kJ/mol) of the electromagnetic radiation. For rigid rotors (no vibration during rotation) and harmonic oscillators (wherein there are equal displacements of atoms on either side of the center of mass) there are simple formulae characterizing the molecular energy levels. In real life, molecules rotate and vibrate simultaneously and high speed rotations affect vibrations and vice versa. However, in our introductory view of spectroscopy we will simplify the picture as much as possible. We will first take up rotational spectroscopy of diatomic molecules.

13.2 Rotational Spectra of diatomics

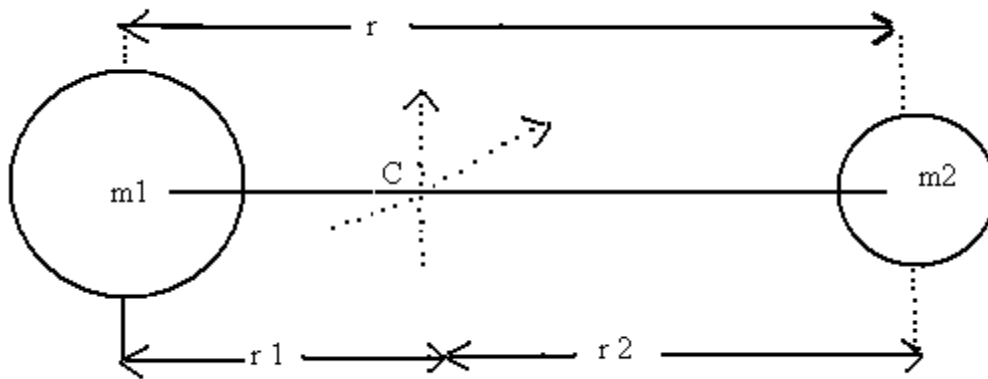Consider a linear rigid diatomic shown in Fig.13.1.

Fig.13.1. A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$ .The centre of mass is at C.

The two independent rotations of this molecule are with respect to the two axes which pass though C and are perpendicular to the "bond length" r. The rotation with respect to the bond axis is possible only for "classical" objects with large masses. For quantum objects, a "rotation" with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$ m_1 \, r_1 = \; m_2 \, r_2 \tag{13.1} $$

The moment of inertia is defined by

$$ I = \; m_1 \, r_1^2 \; + \; m_2 \, r_2^2 \tag{13.2} $$

$$ = \; m_2 \, r_2 \, r_1 \; + \; m_1 r_1 \, r_2 $$

$$ = \; r_1 \, r_2 \; (m_1 + m_2) \tag{13.3} $$

Since $m_1 \, r_1 = \; m_2 \, r_2 \; = \; m_2 \; (r \; - \; r_1)$, $(m_1 + m_2) \, r_1 = m_2 \, r$ Therefore,

$$ r_1 \; = \; \frac{m_2 \, r}{m_1 + m_2} \quad \text{and} \quad r_2 \; = \; \frac{m_1 \, r}{m_1 + m_2} \tag{13.4} $$

Substituting the above equation in (13.3), we get

$$I \; = \; \frac{m_1 \, m_2 \; r^2}{(m_1 \, + m_2 \,)} \; = \; \mu r^2, \quad \mu \; = \; \frac{m_1 \, m_2}{m_1 \, + m_2} \qquad (13.5)$$

Where μ, the reduced mass is given by

$$\frac{1}{\mu} \; = \; \frac{1}{m_1} \; + \; \frac{1}{m_2} \qquad (13.6)$$

The rotation of a diatomic is equivalent to a "rotation" of a mass μ at a distance of r from the origin C. The kinetic energy of this rotational motion is K.E. $= \; L^2/2I$ where L is the angular momentum, $I\omega$ where ω is the angular (rotational) velocity in radians/sec. The operator for L^2 is the same as the operator L^2 for the angular momentum of hydrogen atom and the solutions of the operator equations $L^2 \, Y_{lm} \; = \; l\,(l+1) \, Y_{lm}$, where Y_{lm} are the spherical harmonics which have been studied in lecture 3.

The quantized rotational energy levels for this diatomic are

$$E_J \; = \; \frac{h^2}{8\pi^2 \, I} \; J\,(J+1) \qquad (13.7)$$

The energy differences between two rotational levels is usually expressed in cm^{-1}. The wave number corresponding to a given ΔE is given by

$$\upsilon \; = \; \Delta E \,/hc, \quad cm^{-1} \qquad (13.8)$$

The energy levels in cm^{-1} are therefore,

$$E_J \; = \; B \; J\,(J+1) \quad where \; B \; = \; \frac{h}{8\pi^2 \, Ic} \qquad (13.9)$$

The rotational energy levels of a diatomic molecule are shown in Fig. 13.2.
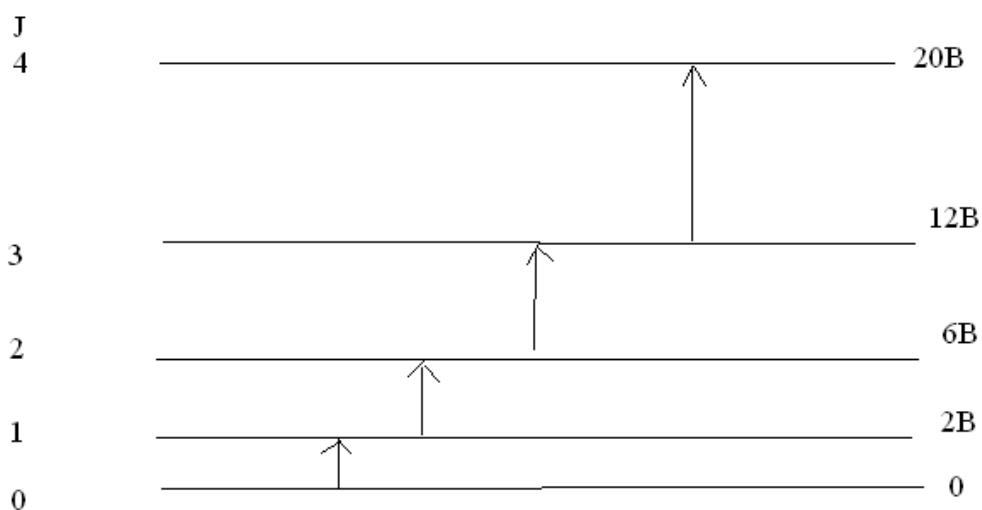
Fig. 13.2 Rotational energy levels of a rigid diatomic molecule and the allowed transitions.

The selection rule for a rotational transition is,

$$\Delta J = \pm 1 \qquad (13.10)$$

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ. Molecules such as HCl and CO will show rotational spectra while H_2, Cl_2 and CO_2 will not. The rotational spectrum will appear as follows
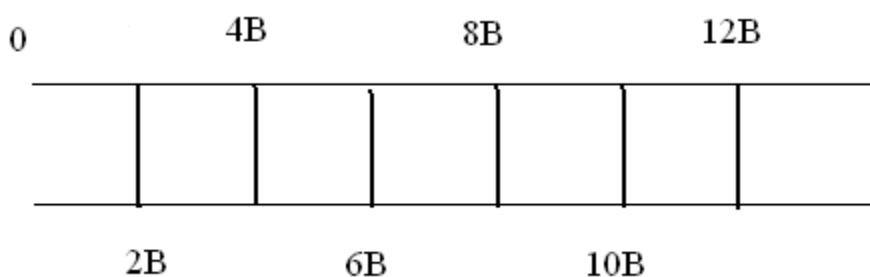

Fig. 13.3 Rotational spectrum of a rigid diatomic. Values of B are in cm^{-1}. Typical values of B in cm^{-1} are 1.92118 (CO), 10.593 (HCl), 20.956 (HF), $^1H_2$ (60.864), $^2H_2$ (30.442), 1.9987 (N_2).

From the value of B obtained from the rotational spectra, moments of inertia of molecules I, can be calculated. From the value of I, bond length can be deduced.

Example 13.1: Calculate the value of I and r of CO. B = 1.92118 cm^{-1}.

Solution:

$I = h/(8\pi^2 \, Bc) \; = \; 6.626 \times 10^{-34}/(8 \times 3.1415^2 \times 1.92118 \times 3 \times 10^{10})$

$= \; 1.45579 \times 10^{-46} \; kg \; m^2$

Since the value of B is in cm^{-1}, the velocity of light c is taken in cm/s. $I = \mu r^2$. The atomic mass of $C \equiv 12.0000$ amu, $O \equiv 15.9994$ amu. 1 amu $= 1.6604 \times 10^{-27}$ kg. The reduced mass of CO can be calculated to be 1.13836×10^{-27} kg.

Therefore $r^2 \; = \; I/\mu = 1.45579 \times 10^{-46}/1.13826 \times ^{-27} \; m^2$

Or $r = 1.131 \; \text{Å}$

The rotational levels are degenerate. Just as there are three p orbitals for l = 1, for J = 1, there are 3 degenerate rotational states. The degeneracy for a given value of J is 2J + 1. The Boltzmann factor gets modified due to this degeneracy as follows

$$N_J/N_J{}' \; = \; [(2J + 1)/(2J' + 1)] \; e^{-\Delta E/k_B T} \tag{13.11}$$

The implication of this is that the rotational population of the J = 1 level is often more than the population of the J = 0 levels since their degeneracies are 3 and 1 respectively. When molecules rotate with great speeds, they cannot be treated as rigid any more. There are distortions due to centrifugal and other forces. The modification of rotational energies by considering the centrifugal distortion alone is

$$E_J \; (\text{in } cm^{-1}) \; = \; B \, J(J+1) - DJ^2(J+1)^2 \tag{13.12}$$

Where the centrifugal distortion constant D is given by

$$D = h^3/(32\pi^4 \, I^2 \, r^2 \, kc) \; cm^{-1} \tag{13.13}$$

The only new term in Eq (13.13) is the force constant k which will be discussed when we study molecular vibrations.

13.3 Rotational Spectra of Polyatomics

Linear molecules such as OCS and $HC \equiv CCl$ have spectra similar to diatomics. In diatomics as well as linear triatomics, $I_A = I_B$; $I_C = 0$. I_A, I_B and I_C are the three moments of inertia of molecules along three independent axes of rotation. Just as any translation can be decomposed into three independent components along three axes such as x, y and z, any rotation can be decomposed into rotations along three axes A, B, and C. The way to choose these axes is to have the simplest values of I_A, I_B and I_C. Since triatomics are heavier than the constituent diatomics, their moments of inertia are larger

and the values of rotational constants, B, are smaller, in the range of 1 cm^{-1}. The value of I_A or I_B determined from the B value gives the total length of the triatomic. To determine the two bond lengths in the linear triatomic, we neede to determine the moment of inertia $I_{A'}$ of an isotope of the triatomic. From two values of I_A and $I_A{}'$, we can determine the two bond lengths.

The rotational spectra of asymmetric molecules for whom $I_A \neq I_B \neq I_C$ can be quite complicated. For symmetric tops, two moments of inertia are equal ie.,

$$I_A = I_B \neq I_C ; \quad I_C \neq 0 \tag{13.14}$$

In CH_3Cl for example, the main symmetry axis is the C – Cl axis. We need two quantum numbers to describe the rotational motion with respect to I_A and I_C respectively. Let J represent the total angular momentum of the molecule and K the angular momentum with respect to the C – Cl axis of the symmetric top. J takes on integer values and K can not be greater than J (recall that $m_l \leq |l|$ for orbital angular momentum). The $(2J + 1)$ "degeneracy" is expressed through the $2J + 1$ values that K can take.

$$K = J, J-1, \ldots 0, \quad -(J-1), -J \tag{13.15}$$

The rotational energies of a symmetric top are given by

$$E_{J,K} / hc = BJ(J+1) + (A-B) K^2, \quad cm^{-1} \tag{13.16}$$

The moments of intertia are related to B and A as

$$B = \frac{h}{(8\pi^2 I_c .c)} \quad \text{and} \quad A = \frac{h}{(8\pi^2 I_A c)} \tag{13.17}$$

As the energy depends on K^2, energies for states with $+ K$ and $- K$ are doubly degenerate. Thus there will be $J + 1$ levels and $(2J + 1)$ states for each values of J.

The selection rules for the symmetric top are,

$$\Delta J = \pm 1 \text{ and } \Delta K = 0 \tag{13.18}$$

It can be easily shown hat

$$(E_{J+1, K} - E_{J,,K})/hc = 2 BJ (J+1) \tag{13.19}$$

This implies that the spectrum is independent of the value of K. The physical meaning is as follows. K refers to the rotation about the symmetry axis such as the C - Cl axis. A rotation about this axis does not change the dipole moment. We mentioned in the section on the rotational spectra of diatomics that the molecular dipole moment has to change during the rotational motion (transition dipole moment operator of Eq 12.5) to induce the

transition. Rotation along the axis A and B changes the dipole moment and thus induces the transition.

By using rotational or microwave spectroscopy, very accurate values of bond lengths can be obtained. For example, in HCN, the C-H length is 0.106317 ± 0.000005 nm and the CN bond length is 0.115535 ± 0.000006 nm. The principle of the microwave oven involves heating the molecules of water through high speed rotations induced by microwaves. The glass container containing water however remains cold since it does not contain rotating dipoles.

13.4 Vibrations and Rotations of a diatomic

You have noticed in your earlier studies that simple pendulums or stretched strings exhibit simple harmonic motion about their equilibrium positions. Molecules also exhibit oscillatory motions. A diatomic oscillates about its equilibrium geometry. The quantized vibration energies E_υ of a harmonic oscillator are

$$E_{\upsilon} = (\upsilon + \tfrac{1}{2})\, h\nu \qquad\qquad (13.20)$$

$$\upsilon = 0,1,2, \ldots\ldots\ldots$$

The vibrational frequency ν is related to the force constant k through

$$\nu = \frac{1}{(2\pi)} \sqrt{\frac{k}{\mu}}, \quad Hz \qquad\qquad (13.21)$$

The vibrational motion occurs under the action of a binding potential energy. The potential energy (PE) curve for a harmonic oscillator is given in Fig. 13.4.
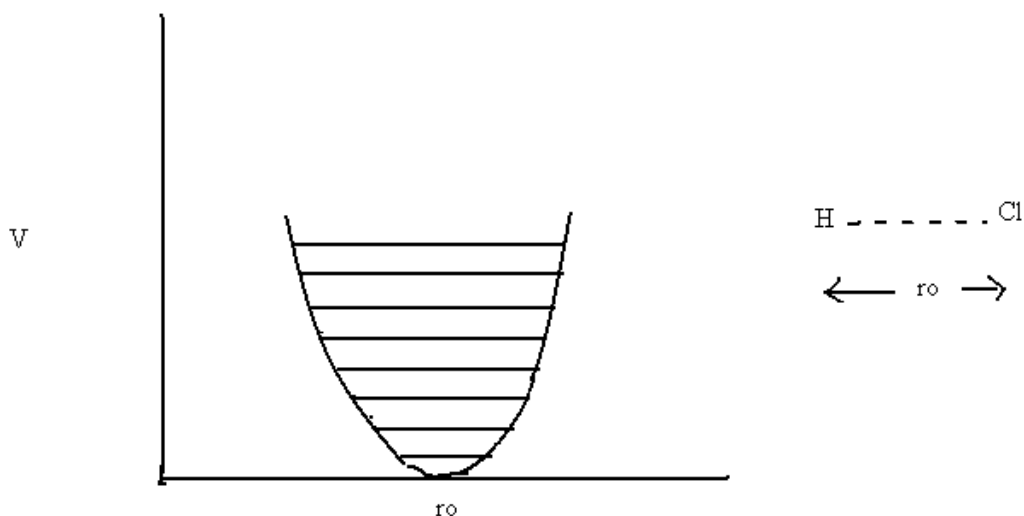
Figure 13.4. The potential energy of a harmonic oscillator $V = k(r-r_o)^2$. The force constants k in N/m for a few moleculues are, CO (1902), HF (966), HCl (516), HI (314).

On either sides of the equilibrium bond length r_o, the PE rises as a symmetric quadratic function (a parabola). The vibrational wavefunctions can be obtained by solving the Schrodinger equation. The Hamiltonian operator (for energy) now consists of a kinetic energy term and a potential energy term V as shown in Fig. 13.4 and the solutions for energy, E_υ have already been given in Eq.(13.20). The selection rules for the harmonic oscillator are:

$$\Delta\upsilon = \pm 1 \tag{13.22}$$

We will see several equally spaced lines (spacing hv) corresponding to the transitions 0→1, 1→2, 2→3 and so on. The first transition will be the most intense as the state with $\upsilon = 0$ is the most populated.

In actual diatomics, the potential is anharmonic. A good description of an anharmonic oscillator is given by the Morse function.

$$\text{P.E.} = D_{eq} [1 - \exp \{a(r_o\text{-}r)\}]^2 \tag{13.23}$$

In Eq. (13.22), D_{eq} is the depth of the PE curve and r_o is the bond length. A plot of the Morse curve and the energy levels for the Morse potential are given in Fig. 13.5. The formula for the energy levels of this anharmonic oscillator is

$$E_v/hc = \varepsilon_v = (v+ \tfrac{1}{2})\, v - (v+ \tfrac{1}{2})^2 v\, x_e, \ \ cm^{-1} \tag{13.24}$$

Here x_e, is called the anharmonicity constant whose value is near 0.01. It can be easily deduced from the above formula that the vibrational energy levels for large υ start bunching together.
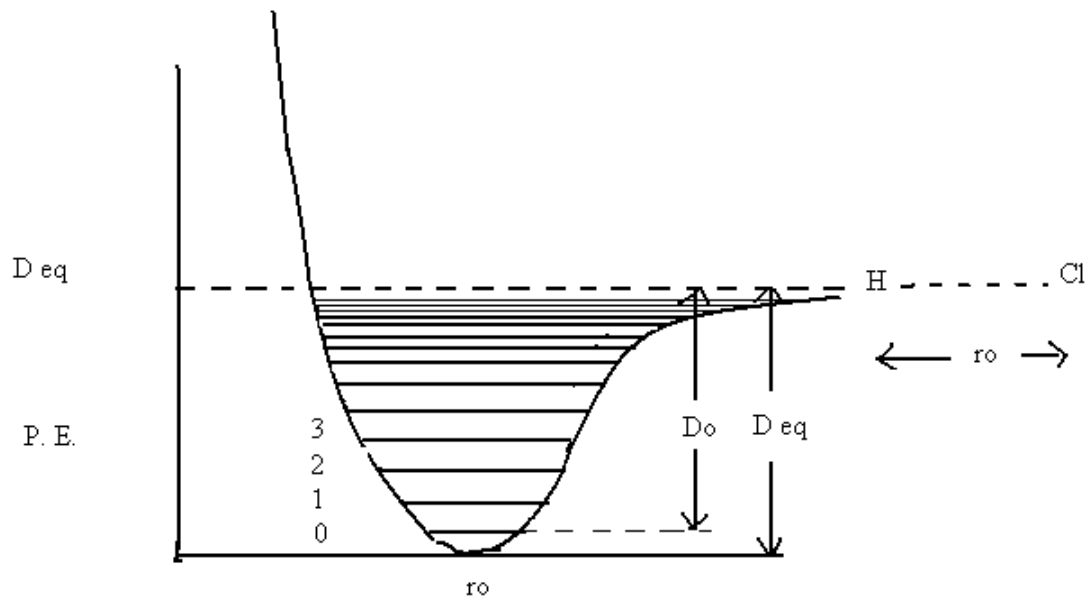
Fig. 13. 5. The Morse potential and the energy levels therein. Note the difference between the dissociation energy D_o and the depth D_{eq}. All molecules have a minimum of the zero point energy of $h\nu/2$ corresponding to the $\nu = 0$ state. This is a consequence of the uncertainty principle!

Often, one observes a combined vibrational rotational spectrum. A combined set of vibrational and rotational energy levels of a diatomic is given by

$$E_{total} = BJ(J+1) + (v + \tfrac{1}{2})\nu - x_e(v + \tfrac{1}{2})^2\nu, \quad cm^{-1} \qquad (13.25)$$

The energy level diagram and the spectrum corresponding to the diagram are shown in Fig. (13.6).
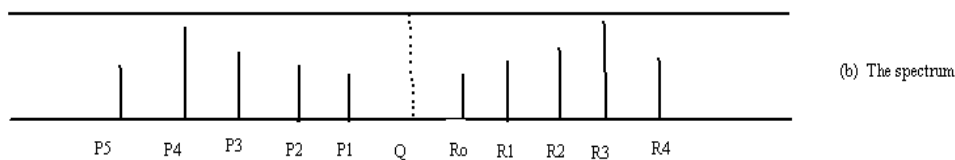

(a) Emergy Levels

(b) The spectrum

| P5 | P4 | P3 | P2 | P1 | Q | Ro | R1 | R2 | R3 | R4 |
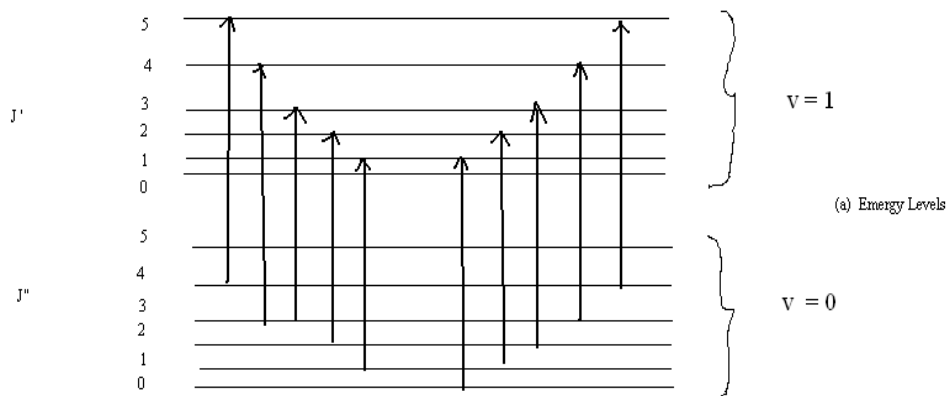
Fig. 13.6. The vibrational rotational spectrum. The selection rules are $\Delta \upsilon = \pm 1, \pm 2, \ldots$ $\Delta J = \pm 1$. $\Delta J = 1$ corresponds to the R branch on the right at higher frequencies and $\Delta J = J'' - J' = -1$ corresponds to the P branch on the left. The dashed line Q for which $\Delta J = 0$, is not seen. The difference between R_0 and P_1 is 4B and the difference between adjacent R lines and adjacent P lines is 2B.

13.5 Vibrational spectra of Polyatomics

An atom moving in three dimensions has three degrees of freedom corresponding to the freedom in movement in, say, the x, y and z directions. A collection of N unabound atoms will have 3N degrees of freedom. If the N atoms are bound through the formation of a molecule, the 3N degrees of freedom get redistributed into translational rotational and vibrational modes. Since the molecule can be translated as a unit, there are three translational modes (degrees of freedom). Similarly there are three rotational modes with respect to three independent axis of rotation. The remaining, 3N-6 are the vibrational modes. For a linear molecule, since there are only two rotational modes with respect to the two axes perpendicular to the molecular axis, there are 3N-5 vibrational modes.

If the potentials energy functions for all the motions can be assumed to be harmonic, then the 3N-6 modes can be categorized into 3N-6 normal modes. Consider the example of water. There are three atoms and 3N-6 = 3 normal modes. In terms of the potential energy functions for vibrations, there are three functions: one each corresponding to each O-H bond and one corresponding to the H-O-H bending. In terms of the individual bond vibrations, the vibrational motion can appear quite complex. The total potential energy P.E. may be written as:

$$\text{P.E.} = \tfrac{1}{2} k \, (r_1 - r_{10})^2 + \tfrac{1}{2} k \, (r_2 - r_{20})^2 + \tfrac{1}{2} k (\theta - \theta_0)^2 \tag{13.25}$$

Here, r_{10} and r_{20} are the equilibrium bond lengths of the two O-H bonds and θ_0 is the equilibrium bond angle. A normal mode of vibration is defined as a vibration in which all atoms oscillate with the same frequency and pass through their equilibrium positions at the same time. The center of mass is unchanged during a normal mode. The three normal modes of vibration of water are shown in the following figure.
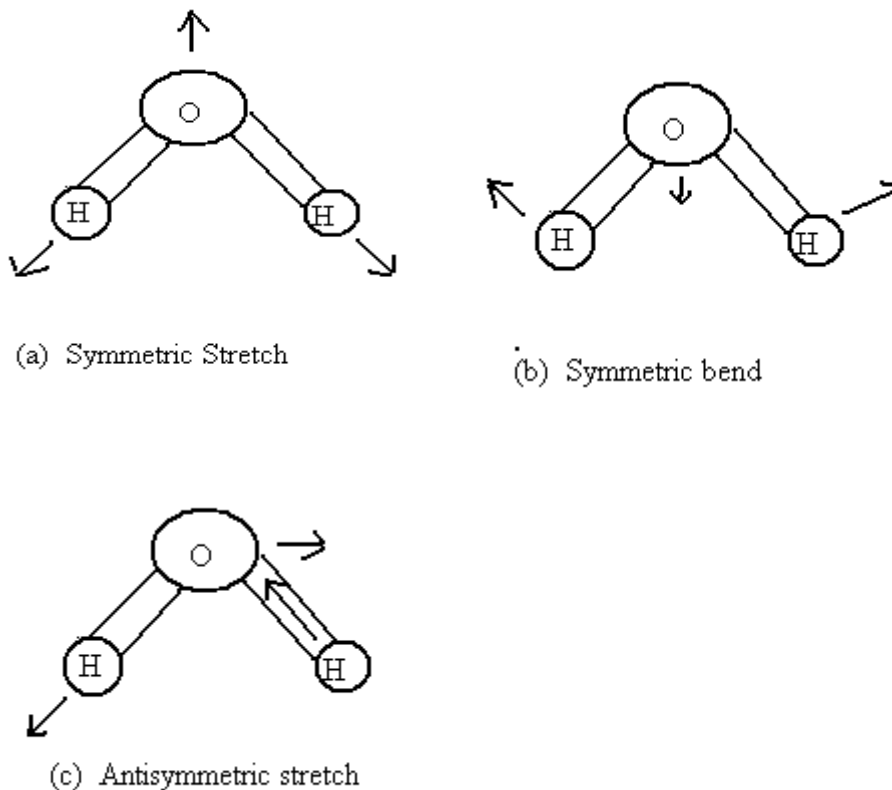
(a) Symmetric Stretch

(b) Symmetric bend

(c) Antisymmetric stretch

Figure 13.7 Normal modes of vibrations of water

The three normal modes of vibrations of water (Fig 13.7) are the symmetric stretch ($v_1 = 3651.7$ cm^{-1}), the antisymmetric stretch ($v_2 = 3755.8$ cm^{-1}) and the symmetric bend ($v_3 = 1595.0$ cm^{-1}). Bending requires less energy and thus, its frequency is lower. The asymmetric stretch requires greater reorganization than the symmetric stretch and hence a larger frequency. Molecular CO_2 is a linear triatomic and has 3N - 5 = 4 normal modes of vibration. The symmetric stretch ($v_1 = 1330$ cm^{-1}) asymmetric stretch ($v_2 = 2349.3$ cm^{-1}) and bending ($v_3 = 66.3$ cm^{-1}) are shown in Fig 13.8. The bending mode is doubly degenerate, owing to the two independent bending modes in two perpendicular planes containing the molecular axis.
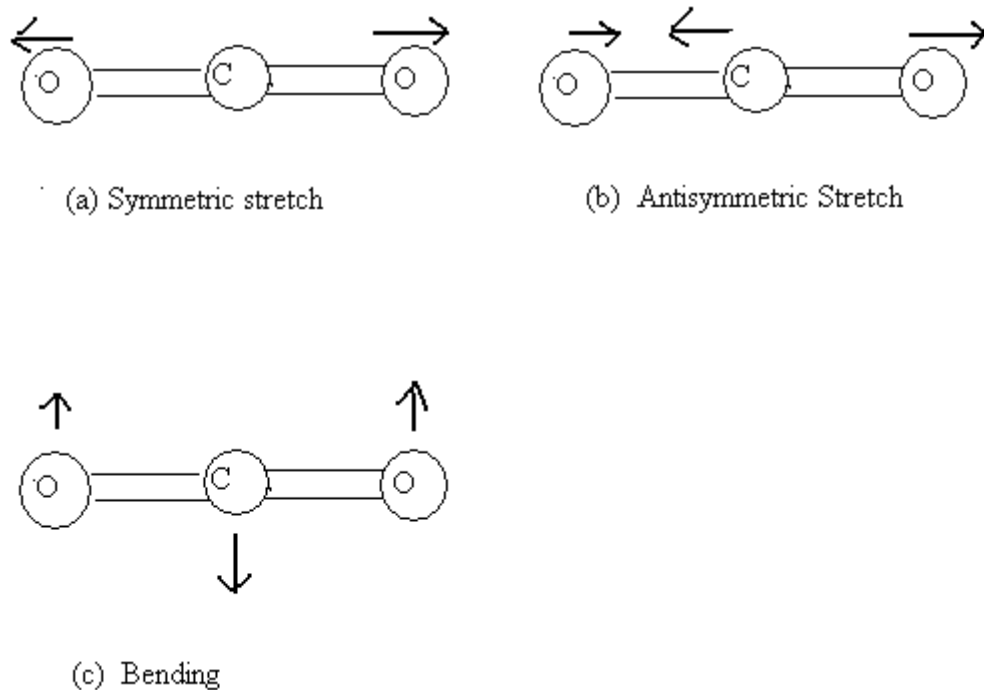
(a) Symmetric stretch

(b) Antisymmetric Stretch

(c) Bending

Figure 13.8 Normal modes of vibrations of CO_2

Different molecules can be easily identified by their normal mode frequencies. In addition to these modes, overtones ($2\upsilon_1$, $3\upsilon_2$, etc.), combination bonds ($\upsilon_1 + \upsilon_2$, $2\upsilon_1 + \upsilon_2$, $\upsilon_1 + \upsilon_2 + \upsilon_3 \ldots$), and difference bonds ($\upsilon_1 - \upsilon_2$, $\upsilon_1 + \upsilon_2 - \upsilon_3$) can be observed. Since a large number of rotational and vibrational levels are closely spaced they provide a rich base for setting up lasers when the upper levels are populated. As in the case of diatomics, rotational lines are richly dispersed in vibrational spectra of polyatomics. The concept of normal modes can be extended to solids and liquids too. Since in a solid, there are a very large number of atoms (of the order of Avogadro number), there are 3N-6 normal modes. These are characterized as phonons, which correspond to collective motions of atoms in a solid.

13.6 Analysis by IR Spectroscopy

IR spectroscopy has grown into an extremely versatile analytical tool. Most organic and inorganic groups (such as CH_3, -C=C, M-C≡0) have characteristic frequencies and these frequencies provides finger prints, using which the groups in newly synthesized molecules can be identified. Although we can not "see" molecules, through various spectral methods, we can identify atoms, groups, bond lengths, relative locations (cis/trans, endo/exo) and so on. The IR frequencies of a few common groups are given in Table 13.2.

Table 13.2 Characteristic frequencies (in cm^{-1}) of some molecular groups.

Group	Approximate frequency	Group	Approximate frequency
C-I	550	$-C \equiv C -$	2200
C-Cl	725	$-C \equiv N$	2250
C=S	1100	S – H	2580
C-O-	1000 – 1200	$-CH_2$	2930 (asym stretch)
			2860 (sym stretch)
C-N	1000 – 1200		1470 (deformation)
C-C	1000 – 1200	$= CH_2$	3030
C=N-	1600	Aromatic C-H	3060
C = C	1650	$\equiv C - H$	3300
C = O	1600 – 1750	$-N-H_2$	3400
		O-H	3600
		H-bonds	3200 – 3570

In special conformations, the group frequencies can deviate from the values in the table significantly.

13.7 Problems

13.1 Which of the following molecule exhibit rotational and/or vibrational spectra/(or microwave and infrared active)?

H_2, HF, CO_2, OCS, CS_2, I_2, NH_3, CH_4, and benzene.

13.2. From the value of B given for H_2 calculate its bond length.

13.3. For HCl, $B = 10.593$ cm^{-1} and the centrifugal distortion constant $D = 0.00053$ cm^{-1}.   Calculate the first four rotational levels. Calculate the force constant for HCl from the value of D.

13.4. Derive the formula $\Delta E_{rot} = E_{J+1}\text{-}E_J = 2B(J+1) - 4D(J+1)^2$ from the formula for E_{J+1} and E_J.

13.5. A cylinder has a moment of inertia I with respect to its cylinder axis while H_2 and N_2 have I = 0 w.r.t. the molecular axis. Justify.

13.6. What are the differences between the harmonic oscillator potential $\frac{1}{2}kx^2$ and the Morse potential? What is the value of PE for the Morse function for r = 0 and $r = \infty$?

13.7. Calculate the number of normal modes of vibrations for the molecules listed in problem 13.1.

13.8. Why is the Q branch not seen in the vibrational rotational spectrum?

13.9. Sketch qualitatively the vibrational spectrum of HCl and $(CH_3)_2$ C = 0.

13.10. What is the ratio of force constants of H_2 and D_2 ? What differences in spectra of $^1H^{37}Cl$, $^2D^{35}Cl$, and $^2D^{37}Cl$ will you observe when these spectra are compared to the spectrum of $^1H^{35}Cl$?

13.8. Summary

In the present lecture, we have explored some of the main features of rotational and vibrational spectroscopy. The quantization of both these energy levels was outlined. The selection rules are $\Delta J = \pm 1$ and $\Delta \upsilon = 1,2,3\ldots$ Rotational Spectroscopy gives the values of rotational constants B, using which bond lengths can be calculated. Introduction of non-rigidity in a rotor or anharmonicity in a harmonic oscillator leads to the bunching of higher energy levels. The rotational vibrational spectra of polyatomics

give rise to the P, Q and R branches. Vibrations of polyatomics can be conveniently studied in terms of the 3N-6 normal modes. In complex molecules, different groups absorb at different characteristic frequencies and these frequencies (Table 13.2) can be used to identify groups in molecules. Thus IR spectra are very useful in qualitative and quantitative analysis.